



# Process Development for Reactive-Ion Etching of Molybdenum (MoS<sub>2</sub>) Utilizing a Poly(methyl methacrylate) (PMMA) Etch Mask

by Alin Cristian Chipara, Alexander L Mazzoni, Robert A Burke, Barbara M Nichols, Matthew L Chin, Sina Najmaei, Eugene Zakar, and Madan Dubey

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# Process Development for Reactive-Ion Etching of Molybdenum (MoS<sub>2</sub>) Utilizing a Poly(methyl methacrylate) (PMMA) Etch Mask

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# **Contents**

List	of Fig	iv	
List	of Ta	ables	v
Ack	now	ledgments	vi
1.	Intr	oduction	1
2.	Met	thods/Procedures	2
3.	Res	ults	3
	3.1	PMMA Age and Composition	4
	3.2	RIE Treatment	5
	3.3	MoS <sub>2</sub> Etch Capability	7
	3.4	Post-Etch Treatments	7
	3.5	Secondary Oxygen RIE	9
	3.6	Mechanism Discussion	11
4.	Con	clusion	12
5.	Ref	erences	14
List	of Sy	mbols, Abbreviations, and Acronyms	16
Dist	tribut	ion List	17

# **List of Figures**

Fig. 1	CAD drawings of the PMMA mask used during the RIE etch step. The hashed area represents where the PMMA would be removed during resist development, whereas the middle areas would remain for the etching process
Fig. 2	a) AFM height profile of the PMMA flap and b) the RMS roughness for the fully etched region (0.17 nm) and the flap (0.52 nm). After zooming in on the PMMA residue, pebbling can be seen in b) the height and phase AFM images. c) Diagram illustrating the incoming reactive ions interacting with the top layer of the PMMA and graphitizing it. d) Optical image of a device with PMMA residue 4
Fig. 3	AFM images of the PMMA residue after CF <sub>4</sub> + O <sub>2</sub> RIE using different PMMA types and ages. The zoomed-in areas in a, b, and c show the PMMA residue agglomerations in the corners of the features. The AFM of PMMA 495 A8 in b shows bending and folding in the smaller rectangular mesa region. The SiO <sub>2</sub> control is shown in d
Fig. 4	Optical imaging after RIE and PMMA removal for $CF_4 + O_2$ , $Cl_2 + O_2$ , and $O_2$ RIE recipes. The left column shows zoomed-in features of the profile from the CAD drawing in Fig. 1. The outlined areas show the remaining residue after the RIE step. The right column shows a broader view for the $CF_4 + O_2$ and $Cl_2 + O_2$ recipes to emphasize the severity of the resist residue
Fig. 5	Etching of MoS <sub>2</sub> using various recipes. Recipe shown at the top. Optical images show the same area before and after RIE etching. Different MoS <sub>2</sub> thicknesses were etched and analyzed
Fig. 6	AFM analysis of different post-etch cleaning recipes and their effect on the PMMA residue. The cleaning procedure is written above each set of AFM images, and the RIE recipe is identified on the image in white text. New PMMA 950 A4 was used for all samples. The samples were cleaned in a) room temperature acetone and imaged with AFM, then the same sample was cleaned in b) hot acetone and imaged again. Then the sample was cleaned in c) hot 1165 and imaged with AFM. With the $Cl_2 + O_2$ sample, the PMMA folded over on top of itself 9
Fig. 7	Effects of a secondary 5-s, 15-sccm, 250-W $O_2$ RIE cleaning step on the a) $CF_4 + O_2$ recipe and b) $Cl_2 + O_2$ recipe. c) $\sigma_{RMS}$ for various treatments

Fig. 8 Schematic of the proposed PMMA residue formation process. Development after EBL exposure will remove an area of PMMA on the chip. Then, as the sample is bombarded by reactive ions, a graphitized PMMA layer is formed. The acetone wash then penetrates through the PMMA and removes the underlying PMMA; however, it is unable to remove the graphitized residue that remains attached to the surface. The residues will remain on the top of the sample and will fall onto the surface depending on how it is removed from the solvent bath. After the residue dries on the substrate it is difficult to remove. 12

#### **List of Tables**

# **Acknowledgments**

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Alin Cristian Chipara and Alexander L Mazzoni contributed equally as co-first authors for this report.

#### 1. Introduction

Our work at the US Army Research Laboratory (ARL) explores the use of 2-D materials in electronic devices. The fabrication of these devices requires several steps including growth, transfer, lithography, dry etching, and metal deposition. Throughout each step the 2-D material is exposed to a variety of chemicals and polymers. Chemical residues and impurities can act as scattering centers, and impurity scattering is often the dominant mechanism that limits mobility in 2-D materials. Therefore, to optimize the electrical properties of the devices, such as doping or mobility, it is important to continuously improve our fabrication processes.

Our current transistor fabrication process relies on poly(methyl methacrylate) (PMMA) for the material transfer off of the growth substrate and for patterning of regions that undergo dry etching and metal lift-off. Previously it has been shown with graphene that the use of PMMA affects the properties of the 2-D layer. For example, the PMMA concentration of the film used to transfer graphene was demonstrated to be important, with higher (lower) concentrations of PMMA leading to higher (lower) p-doping, lower (higher) mobility, and more (less) surface roughness.<sup>3</sup> Pirkle et al. showed that due to incomplete PMMA removal there were changes in the I<sub>2D</sub> to I<sub>G</sub> peak intensity ratio in graphene that led to lowered carrier mobilities and p-type doping of devices.<sup>4</sup> To remove PMMA residue, annealing in a vacuum or forming gas environment is commonly used. However, PMMA removal requires going to temperatures in excess of 300 °C, which has been demonstrated to p-dope graphene<sup>5</sup> except in ultra-high-vacuum conditions.<sup>4</sup> Unfortunately, there is usually still some residue after annealing,<sup>6</sup> and for applications with flexible substrates this heat treatment is often not allowed.

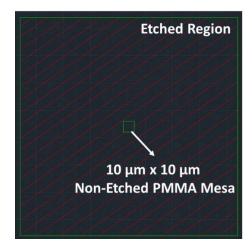
Since polymer interaction with 2-D layers often leads to residues that are difficult to remove, a variety of other methods have been explored to create cleaner devices. For example, researchers have suspended the 2-D channel and performed current annealing,<sup>7</sup> investigated hexagonal boron nitride as an alternative substrate,<sup>8</sup> and developed cleaner pick-up and stack techniques for exfoliated flakes of van der Waals materials.<sup>9</sup> Unfortunately, these techniques are not feasible or developed sufficiently for large-area, batch-processed devices. Current fabrication processing techniques for large-area 2-D materials still often rely on polymers such as PMMA for lithography steps of device fabrication or to perform material transfer from the growth substrate.

Our process for fabricating transistors out of molybdenum disulfide (MoS<sub>2</sub>) grown in-house via chemical vapor deposition (CVD) includes the dry-etching of MoS<sub>2</sub> through a PMMA pattern. Previously we have relied on a carbon tetraflouride (CF<sub>4</sub>) + oxygen (O<sub>2</sub>) reactive-ion etch (RIE) recipe (15 sccm CF<sub>4</sub>, 5 sccm O<sub>2</sub>, and 200 W) to etch MoS<sub>2</sub>. However, we have observed that this process can leave a significant amount of PMMA residue on the substrate surface if the PMMA removal process is not aggressive enough. Additionally, this CF<sub>4</sub> + O<sub>2</sub> process etches silicon dioxide (SiO<sub>2</sub>), which is typically used as both the substrate and back-gate dielectric of our 2-D field effect transistors. The PMMA residue tends to form a flap at the edge of the etched region instead of PMMA particulate matter that is commonly reported in the 2-D literature. While this may not come into contact with the channel region, it can still have drawbacks on the overall device reliability. The goal of this report is to investigate the origin of the PMMA residue and develop a new RIE recipe that eliminates or minimizes the polymer residue and etching of the SiO<sub>2</sub> substrate.

# 2. Methods/Procedures

To investigate the residue issue we fabricated several PMMA mesa structures and performed test etches while varying the PMMA age, composition, RIE gases, as well as the PMMA removal process.

Computer aided design (CAD) drawings of the test patterns used are shown in Fig. 1. Each structure consisted of a large square ( $200 \times 200 \ \mu m$ ) that would be etched and an inner protected region that was either a small square ( $10 \times 10 \ \mu m$ ) or rectangle ( $1 \times 5 \ \mu m$ ). A square and a rectangle were chosen to compare the 2 geometries and determine if their dimensions impacted the etching process.



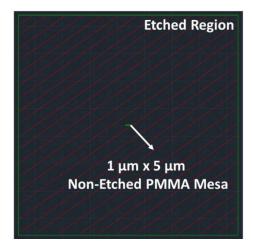


Fig. 1 CAD drawings of the PMMA mask used during the RIE etch step. The hashed area represents where the PMMA would be removed during resist development, whereas the middle areas would remain for the etching process.

For all patterning, the PMMA was spun at 2000 rpm and baked on a hot plate at 180 °C for 2 min to cure the resist. All patterning of PMMA was done via electron beam lithography (EBL; Vistec EBPG5000+) with an exposure dose of 850  $\mu$ C/cm<sup>2</sup> and development in 25 mL of isopropyl alcohol (IPA): 10 mL methyl isobutyl ketone for 75 s.

The standard RIE (performed using an Ulvac NE550e) step consisted of a 200-W, 45-s, 15-sccm CF<sub>4</sub>, and 5-sccm O<sub>2</sub> etch. After etching, PMMA was removed by an overnight soak in acetone followed by an IPA rinse and drying with nitrogen.

The topography of our samples was investigated via atomic force microscopy (AFM) using a Veeco Nanoman V in tapping mode.

#### 3. Results

Our devices exhibited flap-like structures around the dry-etched area, which we attributed to the PMMA etch mask hardening during our standard RIE process (Fig. 2). This residue is very similar to that observed by Koval et al. <sup>10</sup> and Oehrlein et al. in terms of topography and size. <sup>11</sup> Other papers have shown that the use of RIE can cause the PMMA to exhibit pebbling and become difficult to remove. <sup>11</sup> AFM revealed the flaps to be about 5 nm thick with a pebble-like structure. Oehrlein et al. suggested that the reason for this is the graphitization of the top layer of the PMMA due to the energy of the reactive ions interacting with the surface layer (Fig. 2). <sup>11</sup>

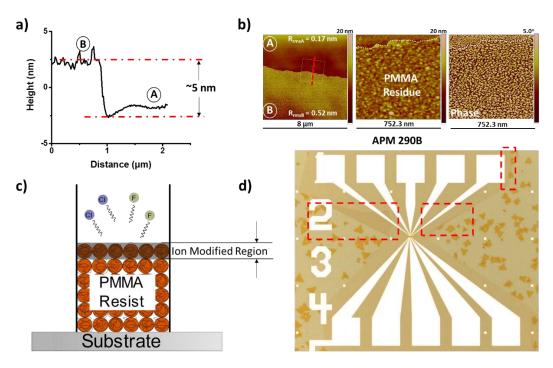


Fig. 2 a) AFM height profile of the PMMA flap and b) the RMS roughness for the fully etched region (0.17 nm) and the flap (0.52 nm). After zooming in on the PMMA residue, pebbling can be seen in b) the height and phase AFM images. c) Diagram illustrating the incoming reactive ions interacting with the top layer of the PMMA and graphitizing it. d) Optical image of a device with PMMA residue.

# 3.1 PMMA Age and Composition

In our initial experiments, we investigated different types of PMMA (950 A4 and 495 A8) and different ages of PMMA 950 A4 (2006 vs. 2017) to determine if PMMA type or age affects the etching process. The numbers 950 and 495 refer to the molecular weight of the PMMA (950,000 and 495,000, respectively). A4 and A8 refer to the concentration of the PMMA in the solvent anisole (4% and 8% in anisole, respectively). Higher molecular weight and PMMA concentrations create a more viscous fluid that, when spin-coated, results in a thicker film.

To explore the impact of the PMMA age and composition, we used AFM to image the mesas after RIE of the regions. The age of the PMMA did not appear to have a noticeable effect on the resulting mesa (Figs. 3a and c), but there was a significant difference in the final mesa topography when using 950 A4 versus 495 A8 (Figs. 3a and b). Both PMMA A4 and A8 were spun at 2000 rpm (300 nm for A4 and 650 nm for A8), but PMMA A8 led to warping of the patterned structures due to a significant increase in viscosity compared with A4. However, all of the PMMA compositions exhibited PMMA agglomerations at the corners of the mesa regions, which could contribute to contamination and strain in devices among other negative

effects. Since the A8-based samples were warped, we chose to use the new PMMA 950 A4 as our standard for the all later experiments such as varying the RIE recipe or removal processes.

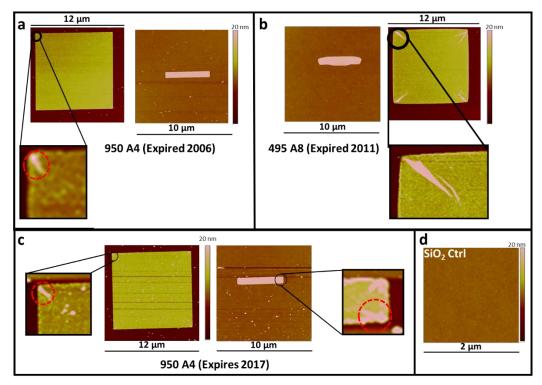


Fig. 3 AFM images of the PMMA residue after  $CF_4 + O_2$  RIE using different PMMA types and ages. The zoomed-in areas in a, b, and c show the PMMA residue agglomerations in the corners of the features. The AFM of PMMA 495 A8 in b shows bending and folding in the smaller rectangular mesa region. The  $SiO_2$  control is shown in d.

#### 3.2 RIE Treatment

After determining the effects of the PMMA type and age, we started optimizing the RIE parameters in an attempt to resolve the PMMA residue issue. We tested several RIE gas chemistries including our CF<sub>4</sub> + O<sub>2</sub> standard (15 sccm CF<sub>4</sub> + 5 sccm O<sub>2</sub> for 45 s at 200 W), chlorine (Cl<sub>2</sub>) + O<sub>2</sub> (15 sccm Cl<sub>2</sub> + 5 sccm O<sub>2</sub> for 45 s at 200 W), and O<sub>2</sub> (15 sccm, 20 s at 200 W + 20 s at 250 W). The O<sub>2</sub> recipe failed midway through the process, which is why there are two 20-s steps, one at 200 W and another at 250 W. Since we saw the residue flaps using CF<sub>4</sub> + O<sub>2</sub>, it was designated as our control sample. Cl<sub>2</sub> was chosen as one of the alternative chemistries since it does not etch the SiO<sup>2</sup> layer, which is important for device reliability since it minimizes leakage effects. O<sub>2</sub> was picked due to its ability to remove graphitized layers. PMMA 950 A4 was spun onto several SiO<sub>2</sub>/Si chips, and the pattern from Fig. 1 was written using EBL. After developing the resist, each chip was exposed to a different RIE gas chemistry. After an overnight soak in acetone, followed by

an IPA rinse and drying the sample with nitrogen, optical microscopy and AFM were performed on the chips. The optical images in Fig. 4 show that both the  $CF_4$  +  $O_2$  and  $Cl_2$  +  $O_2$  etch recipes produce flaps and exhibit large amounts of PMMA residue, while  $O_2$  leaves little to no residue. The  $CF_4$  +  $O_2$  etch exhibits less residue than the  $Cl_2$  +  $O_2$  etch, but it did remove some of the oxide layer unlike the  $Cl_2$  +  $O_2$  etch.

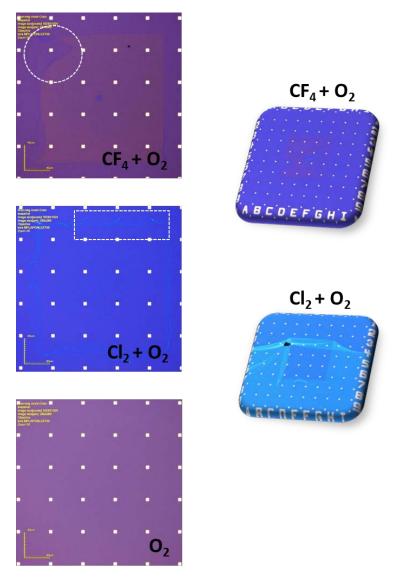


Fig. 4 Optical imaging after RIE and PMMA removal for  $CF_4 + O_2$ ,  $Cl_2 + O_2$ , and  $O_2$  RIE recipes. The left column shows zoomed-in features of the profile from the CAD drawing in Fig. 1. The outlined areas show the remaining residue after the RIE step. The right column shows a broader view for the  $CF_4 + O_2$  and  $Cl_2 + O_2$  recipes to emphasize the severity of the resist residue.

### 3.3 MoS<sub>2</sub> Etch Capability

While it is important for the RIE recipe to limit hardening of the PMMA and etching of  $SiO_2$ , it is also paramount that it can successfully etch  $MoS_2$ . Therefore, we investigated the  $MoS_2$  etch capability using the different RIE recipes ( $Cl_2 + O_2$  and  $O_2$  chemistries) on material grown by CVD.  $CF_4$  was already known to be capable of etching  $MoS_2$  and served as a benchmark. Initial tests with  $Cl_2 + O_2$  at 200 W (left side, Fig. 5) showed efficient etching of monolayer  $MoS_2$ ; however, thicker areas such as the string-like structures remained. Raising the power of the  $Cl_2 + O_2$  recipe to 250 W successfully removed the thicker areas of  $MoS_2$  (Fig. 5, left side). When etching with  $O_2$  we found it difficult to etch thicker layers of  $MoS_2$  and could only efficiently etch  $MoS_2$  monolayers (Fig. 5, right side).

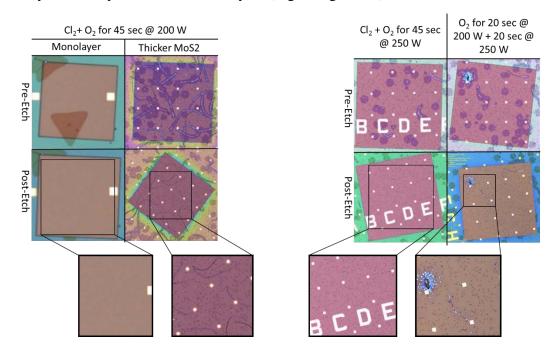


Fig. 5 Etching of  $MoS_2$  using various recipes. Recipe shown at the top. Optical images show the same area before and after RIE etching. Different  $MoS_2$  thicknesses were etched and analyzed.

#### 3.4 Post-Etch Treatments

In an attempt to find a solution for the flaps and mesa region residue, we looked at 2 different approaches: chemical solvents and additional dry etching steps. The first approach relied on post-etch treatments utilizing different solvents and heating of the solvents. Besides room temperature acetone, we also tried heating the acetone to 60 °C, since many researchers have shown improved removal of the resist by heating it. <sup>14,15</sup> We also investigated a heated solution of Microposit Remover 1165

(1-methyl-2-pyrrolidinone, or 1165 for short) as an alternative to acetone. We started with a baseline cleaning by soaking the processed chips (different etch chemistries of  $Cl_2 + O_2$ ,  $CF_4 + O_2$ , and  $O_2$ ) in acetone overnight. We then performed AFM on the cleaned samples, after which we placed them in a hot acetone bath (60 °C) for 1 h. After the soak was complete we carried out AFM again to observe if there were any changes in surface roughness compared with the overnight acetone soak. The final clean involved soaking the samples in 1165 at 60 °C for 1 h. Then we performed AFM to investigate the presence of any changes from the 1165 soak. Hot acetone was found to remove many of the residual surface particles that the overnight soak left behind (Figs. 6a and b). The AFM data, however, showed almost no difference between the hot acetone and 1165 treatments (Fig. 6c). None of the post-etch treatments showed the ability to fully remove the flaps chemically, suggesting that the flaps exhibit a significantly different chemical structure than PMMA. On the other hand, these flaps can be physically removed through excessive heating of acetone (>60 °C), squirting the sample with solvent, or sonication. However, by using these physical procedures, there is a larger risk that the quality and structural integrity of the 2-D layer may be negatively affected.

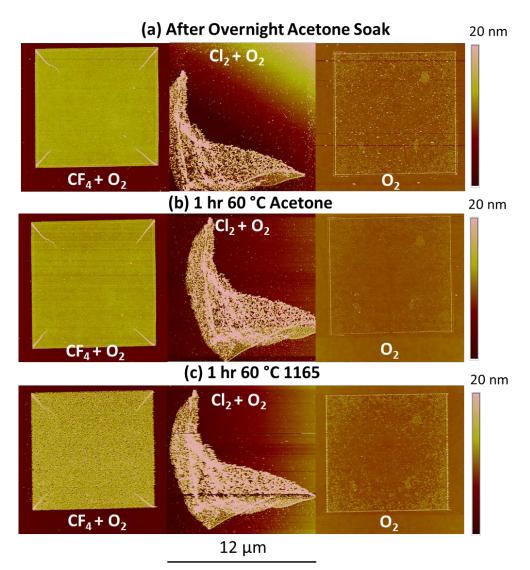


Fig. 6 AFM analysis of different post-etch cleaning recipes and their effect on the PMMA residue. The cleaning procedure is written above each set of AFM images, and the RIE recipe is identified on the image in white text. New PMMA 950 A4 was used for all samples. The samples were cleaned in a) room temperature acetone and imaged with AFM, then the same sample was cleaned in b) hot acetone and imaged again. Then the sample was cleaned in c) hot 1165 and imaged with AFM. With the Cl<sub>2</sub> + O<sub>2</sub> sample, the PMMA folded over on top of itself.

## 3.5 Secondary Oxygen RIE

The second approach to reduce/remove the PMMA residue relied on adding a secondary RIE step that used a pure  $O_2$  recipe (15 sccm, 5 s, at 250 W) to remove the hardened PMMA. As previously mentioned,  $O_2$  should be able to remove any graphitized layer that would form on the surface.<sup>14</sup> The  $O_2$  etch recipe was applied after the initial RIE, and the secondary  $O_2$  step was found to remove the agglomerations in the corners as well as the previously seen flaps for both  $CF_4$  +  $O_2$  and  $Cl_2$  +  $O_2$  etched samples (Figs. 7a and b).

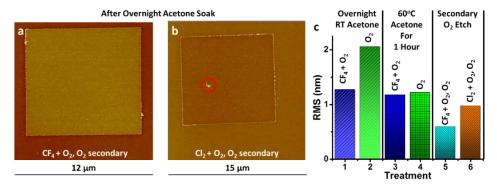


Fig. 7 Effects of a secondary 5-s, 15-sccm, 250-W  $O_2$  RIE cleaning step on the a)  $CF_4 + O_2$  recipe and b)  $Cl_2 + O_2$  recipe. c)  $\sigma_{RMS}$  for various treatments.

We believe that when the O<sub>2</sub> was combined with CF<sub>4</sub> or Cl<sub>2</sub>, residue was observed because the rate of removal of hardened PMMA was lower than the rate at which the CF<sub>4</sub> or Cl<sub>2</sub> hardened the top PMMA layer. To further analyze the data, we looked at the root-mean-square (RMS) surface roughness ( $\sigma_{RMS}$ ) values for the mesa region after undergoing the aforementioned treatments. The AFM data was flattened using the built-in software Nanoscope 7.30. Then the data was exported, and the RMS data for the mesa region was analyzed by drawing a mask over the mesa area with the image software Gwyddion. This allowed us to fully analyze the mesa region and minimize deviations that arise from moving between the etched and nonetched region of the sample. The  $CF_4 + O_2$  etch with the secondary  $O_2$  step showed the best results with an average surface roughness of approximately 0.59 nm (Fig. 7c). However, the  $Cl_2 + O_2$  recipe with the secondary  $O_2$  step also showed very low surface roughness (0.97 nm), which reaches parity with the aforementioned recipe if we neglect the impact of the large residue chunk (Fig. 7b). Compared with previous AFM data taken in this experiment, the largest variability in surface roughness was seen in the O2 recipe with an overnight acetone soak (2.05 nm) (Fig. 7c). It is also clear that hot acetone is much better at removing surface debris than regular acetone as shown by the surface roughness reduction in both the CF<sub>4</sub> + O<sub>2</sub> (7.6% decrease in  $\sigma_{RMS}$ ) samples and the O<sub>2</sub> (40.7% decrease in  $\sigma_{RMS}$ ) etched samples. The room temperature acetone baseline clean exhibits an average roughness of 1.66 nm. By using hot acetone the roughness drops to 1.2 nm with a very small differences between the different etch samples (~3%). Of the etching processes, the best method to minimize surface roughness is using a secondary O<sub>2</sub> etch step. Performing the secondary O<sub>2</sub> etch step reduces the surface roughness further to about 0.78 nm. This implies that the samples undergo a stepwise removal of various particulates (i.e., hot acetone removes more particulates than room temperature acetone but much less than the secondary O<sub>2</sub> etch step). RMS data for the Cl<sub>2</sub> sample are not compared because the residue flaps are large and folded on top of each other, distorting the results.

Table 1 outlines the pros and cons of each gas recipe for etching  $MoS_2$  on  $SiO_2$ . As can be seen, both the  $CF_4 + O_2$  and the  $Cl_2 + O_2$  recipes are suitable for etching thicker  $MoS_2$ ; however, they also harden the PMMA mask, which can lead to the observed residue. Additionally,  $CF_4 + O_2$  has been shown to etch  $SiO_2$ , while  $Cl_2 + O_2$  does not etch the oxide layer. The pure  $O_2$  recipe cannot etch thicker  $MoS_2$  and does not etch the oxide layer. To achieve all the desired results for our mesa etch, the  $Cl_2 + O_2$  etch with a secondary  $O_2$  step was chosen (Table 1, last column).

Table 1 Comparison of different RIE gas chemistries

Effect	$\mathbf{CF_4} + \mathbf{O_2}$	$Cl_2 + O_2$	O <sub>2</sub>	$CF_4 + O_2, O_2$	$Cl_2 + O_2, O_2$
Etches monolayer MoS <sub>2</sub>	✓	✓	✓	✓	✓
Etches multilayer MoS <sub>2</sub>	$\checkmark$	$\checkmark$	×	$\checkmark$	$\checkmark$
Does not etch SiO <sub>2</sub>	×	$\checkmark$	$\checkmark$	×	✓
No hardened PMMA	×	×	$\checkmark$	$\checkmark$	$\checkmark$
residue					

#### 3.6 Mechanism Discussion

The schematic in Fig. 8 shows the expected mechanism for the formation of the PMMA flaps and residue. Initially, we start with a PMMA-coated substrate that is patterned using EBL to match our CAD design. Next, the RIE process is performed, during which the sample is bombarded by reactive ions. This causes the top layer of PMMA to harden and graphitize. The specific mechanism for the hardening is as yet unknown; however, there are several theories mentioned in papers such as Koval et al. 10 and Oehrlein et al. 11 Most researchers agree that this is not a localized heating issue and is a reaction to the high-energy reactive particles that are impacting the surface. This tends to lead to polymer scission, which exposes reactive sites that can cause hardening or graphitization. After the RIE process, the samples were imaged and showed no residue on the exposed SiO<sub>2</sub> area. Residue is seen only after PMMA removal in solvent. Because of the lack of residue after etching, we believe the meeting points between the substrate, polymer, and etch process act as an anchoring location for the residue itself. As the material is left in an acetone bath, the PMMA that was not graphitized is removed, leaving behind a graphitized PMMA layer that is anchored to the substrate surface. The hardened PMMA layer cannot be removed with room temperature acetone baths and requires sonication/heated acetone (>60 °C) or direct squirting to remove. When the sample is removed from the solvent baths, the flaps adhere to the substrate as the solvents evaporate.

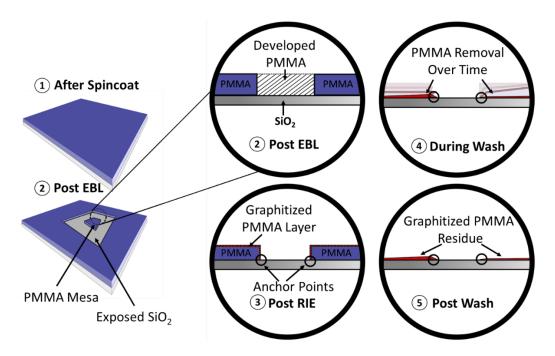


Fig. 8 Schematic of the proposed PMMA residue formation process. Development after EBL exposure will remove an area of PMMA on the chip. Then, as the sample is bombarded by reactive ions, a graphitized PMMA layer is formed. The acetone wash then penetrates through the PMMA and removes the underlying PMMA; however, it is unable to remove the graphitized residue that remains attached to the surface. The residues will remain on the top of the sample and will fall onto the surface depending on how it is removed from the solvent bath. After the residue dries on the substrate it is difficult to remove.

#### 4. Conclusion

We have shown that RIE can lead to PMMA residue in our device fabrication process, since the RIE will graphitize the top layer of PMMA. In our case, the PMMA residue takes the form of a flap rather than as general particulates. If an additional O<sub>2</sub> RIE step is added, the graphitized PMMA can be effectively removed. Other observations from our study include the following:

- The observed residue did not depend on the age (2006 vs. 2017) of the PMMA used; however, it was worse for thicker PMMA films.
- Both CF<sub>4</sub> and Cl<sub>2</sub> RIE processes led to the formation of the residue flaps; however, O<sub>2</sub> processes did not.
- Heated acetone and 1165 were not able to chemically remove the residue, indicating that the flaps left on the wafer surface were significantly modified from the original PMMA structure.

- 1 h of heated acetone (60 °C) demonstrated an improvement in removal of particulate residue compared with an overnight soak in room temperature acetone.
- Both CF<sub>4</sub> and Cl<sub>2</sub> RIE processes could etch thicker regions of MoS<sub>2</sub>; however, O<sub>2</sub> could only etch monolayer regions.
- CF<sub>4</sub> RIE processes etch SiO<sub>2</sub>, which is commonly used as a substrate and back-gate dielectric, whereas Cl<sub>2</sub> and O<sub>2</sub> do not.
- By adding a secondary 5- to 10-s O<sub>2</sub> step to the CF<sub>4</sub> or Cl<sub>2</sub> RIE processes, the residue flaps are completely removed.

Going forward, we are switching from the  $CF_4$  RIE recipe to a  $Cl_2$  process with a secondary  $O_2$  step. This process improvement ensures no hardened PMMA residue will be present and that the  $SiO_2$  substrate and back-gate dielectric will be better protected.

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# List of Symbols, Abbreviations, and Acronyms

1165 Microposit Remover 1165 (1-methyl-2-pyrrolidinone)

 $\sigma_{RMS}$  root-mean-square surface roughness

2-D 2-dimensional

AFM atomic force microscopy

ARL US Army Research Laboratory

CAD computer-aided design

CF<sub>4</sub> carbon tetrafluoride

Cl<sub>2</sub> chlorine

CVD chemical vapor deposition

EBL electron beam lithography

IPA isopropyl alcohol

MoS<sub>2</sub> molybdenum disulfide

 $O_2$  oxygen

PMMA poly(methyl methacrylate)

RIE reactive-ion etching

RMS root mean square

SiO<sub>2</sub> silicon dioxide

- 1 DEFENSE TECHNICAL
- (PDF) INFORMATION CTR DTIC OCA
  - 2 DIR ARL
- (PDF) RDRL DCM

IMAL HRA RECORDS MGMT

RDRL DCL

**TECH LIB** 

- 1 GOVT PRINTG OFC
- (PDF) A MALHOTRA
  - 18 DIR ARL
- (PDF) RDRL DE

T O'REGAN

RDRL SER L

A MAZZONI

M CHIN

R BURKE

M DUBEY

W NOTHWANG

**B NICHOLS** 

E ZAKAR

S NAJMAEI

C KNICK

RDRL SEE

P SUNAL

M ROY

N MARK

RDRL SER E

J WEIL

T IVANOV

G BIRDWELL

P SHAH

F CROWNE

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